THE INFLUENCE OF OSMOTIC PRESSURE
ON POULTICING TREATMENTS

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Abstract

The crystallization of salts is widely recognized as one of the most significant causes of irreversible damage to many cultural objects such as wall paintings, stone sculptures, and historic buildings. The removal of salts from these objects is however difficult and often poultices are used. In these methods a wet poultice is applied to the surface of the substrate to be treated and is kept in place for some period of time before being removed. Many studies up to now on poulticing have focused on the salt and moisture transport solely in terms of advection and diffusion. The objective of this study is to demonstrate the potential contribution of osmotic pressure to salt extraction during poulticing treatments. To this end, we have conducted a series of experiments where we have measured the moisture transport during poulticing for some well-defined materials. Here we have used Nuclear Magnetic Resonance (NMR) to measure non-destructively the moisture transport during these experiments. This study shows that osmotic pressure can exert a significant influence on salt extraction by poulticing methods during drying. Importantly, as salt is transported from the substrate and into the poultice, this results in a build-up of osmotic pressure within the poultice decreasing the effective pore-size of the poultice. Therefore, the build-up of osmotic pressure enhances the salt extraction and thus increases the efficiency of the poulticing treatment.

Keywords: poulticing, osmotic pressure, NMR

1. Introduction

The crystallization of salts in porous media is widely recognized as one of the primary causes of irreversible damage to many cultural objects such as wall paintings, sculpture, historic buildings, and other artworks (Arnold and Zehnder 1991; Goudie and Viles 1997). Moreover, contemporary buildings and civil constructions also suffer from salt-related deterioration processes. Salt crystallization can therefore be regarded as a common deterioration problem with significant cultural and economic implications. Poulticing is a common method used in conservation to reduce the salt content of the affected object (Verges-Belmin and Siedel 2005). The methodology of application is relatively simple: the wet poultice is applied to the surface of the substrate to be treated and is kept in place for some period of time before being removed. The desalination treatment by poultice includes two main phases. The first is the wetting phase: water is transported from the poultice into the wall where it starts to dissolve the salts. Water may penetrate the substrate due to water vapor transport by means of water vapor

diffusion or due to water capillary suction. The second phase is the salt extraction. The dissolved salt ions travel in the form of an aqueous saline solution from the substrate into the poultice. This salt migration can be the result of two different processes. The first is generated by the existence of a concentration gradient between the substrate and the poultice. In this case the salt ions diffuse through the solution. The second is realized by the capillary water flow from the substrate to the poultice (generally due to drying) and is accompanied by ions advection within the solution.

The present research focuses on salt extraction by drying poultices, during which advection is the main mechanism for salt removal. In the case of advection based salt extraction the efficiency of salt extraction is strongly dependent on the relative pore-size range of the substrate and the poultice (Pel et al. 2010). This extraction process is however potentially considerably faster than diffusion based methods. This can to some extent be achieved through the inclusion of clay minerals (such as kaolin) in poultice mixtures (Lubelli and van Hees 2010)

Up to now most studies on poulticing have focused on the salt and moisture transport solely in terms of advection and diffusion. However in salt extraction, as there are salt gradients present so too will there be osmotic pressure gradients, which could have an influence. The aim of the work was to investigate the influence of osmotic pressure on poulticing. First, the fundamental aspects of capillary transport and osmotic pressure relating to a combination of two porous materials drying will be discussed. Then, the NMR method and setup for measuring non-destructively the moisture distribution, during the experiments on the influence of the osmotic pressure in poulticing drying is explained in Section 3. Finally, the results of the experiments showing the influence of the osmotic pressure on the desalination process will be discussed.

2.   Theory

The term 'advection' refers to the transport of mass by a moving medium. In the case of salt extraction by advection, the dissolved ions can be transported by the moisture flow from substrate into the poultice. Advection is generally more rapid than diffusion, and so desalination treatments based on advection can be much faster. However, in order for advection from the substrate into the poultice to take place, certain requirements regarding the pore size distribution of the poultice and of the substrate need to be fulfilled; in particular the poultice must contain a sufficient quantity of pores that are smaller than the majority of those in the substrate (Pel et al. 2010).

2.1 Influence of the capillary pressure

In general the driving force for the transport of water by advection is drying. During drying, the largest pores will empty first, where the capillary pressure (P_c) is lowest, as can be seen from the following equation:

$$P_c = \frac{2\gamma}{r_m}\cos(\varphi) \qquad (1)$$

In this equation r_m is a pore radius that discriminates between the pores filled with water ($r < r_m$) and the empty pores ($r > r_m$), γ [Nm^{-1}] is the surface tension of the liquid/vapor interface and φ is the contact angle between the liquid/air and liquid/solid interface.

In most porous materials the pores are not uniform, and therefore there is a pore size distribution. Hence, in this case the overall macroscopic capillary pressure ψ_c of the material is a function of its pore size distribution. For any moisture content θ [$m^3 m^{-3}$], there will be a critical pore radius, r_m, corresponding to a certain capillary pressure that discriminates between the pores filled with water and the empty pores. Hence, the macroscopic capillary pressure ψ_c is a function of the moisture content θ, which can be described thus:

$$\psi_c = \psi_c(\theta) \quad (2)$$

If we assume a perfect hydraulic contact at the poultice/substrate interface, the capillary pressure will be continuous at this interface, i.e.:

$$\psi_p(\theta_p) = \psi_s(\theta_s) \quad (3)$$

where ψ_p is the capillary pressure of the poultice, ψ_s the capillary pressure of the substrate, and θ_p and θ_s the moisture content of the poultice and substrate at the interface.

Hence, due to differences in the porosity and pore size distribution between the two materials there will be a jump in moisture content across the interface. The relationship between the moisture contents either side of the interface can be described thus:

$$\theta_p = \psi_p^{-1}\psi_s(\theta_s) = f(\theta_s) \quad (4)$$

Hence, in general there will be a jump in moisture content across an interface
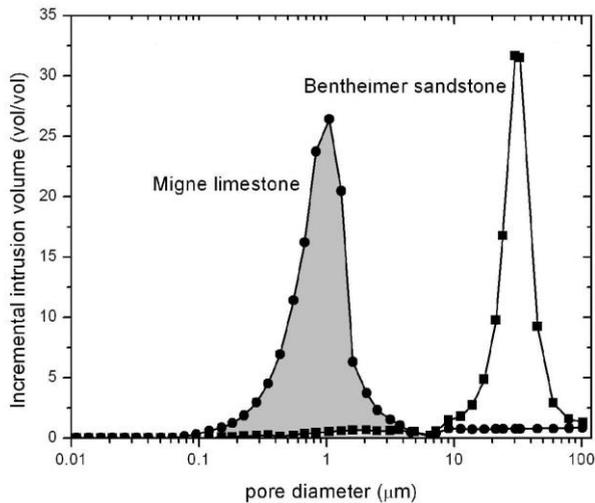
Figure 1. The pores size distribution as obtained by mercury intrusion porosimetry for Migne limestone and Bentheimer sandstone reflecting a fine and a coarse porous material.

As an example reflecting a poultice/substrate combination we can look at the drying of a combination of two materials, i.e., Bentheimer, which is a material with coarse pores, and Migne limestone, which is a material with fine pores. The pore size distribution as measured by MIP for these materials is given in Figure 1.

In Figure 2 the measured moisture profiles are given for the water saturated fine/coarse material combination. As can be seen the measured moisture profiles reflect the pore size distributions. In both cases the material with the largest pores dries first, i.e. the Bentheimer sandstone. These results conform to the general idea that in order to extract salts by advection using drying poulticing methods, the poultice should have pores smaller than that of the substrate (Pel et al. 2010, Sawdy et al. 2010).
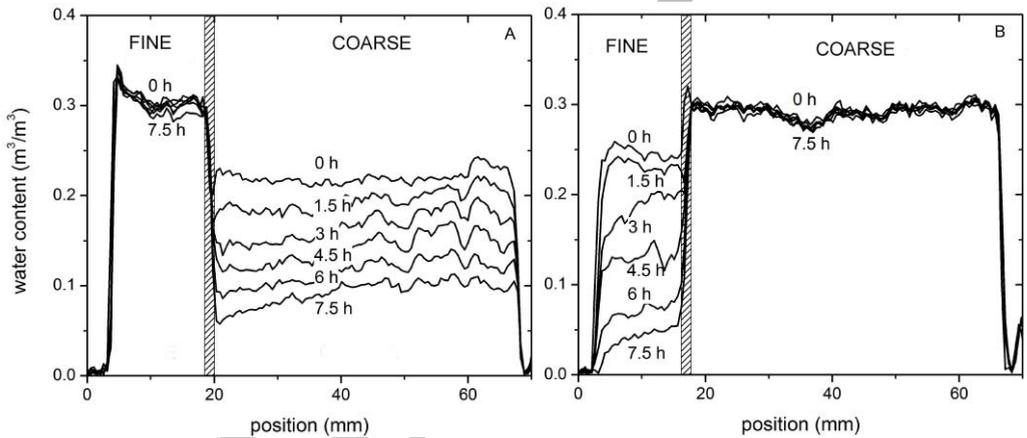
Figure 2. The moisture profiles as measured during drying at various times for a combination of a coarse and fine porous material. The samples are dried at the left side where as the right side is sealed off. As a fine porous material, Migne limestone is used, and as a coarse porous material, Bentheimer sandstone is used.

2.2 Influence of the osmotic pressure

When the substrate/poultice system contains a saline solution there will be an additional contribution to the macroscopic capillary pressure due to the osmotic pressure for each material, i.e.:

$$\psi = \psi_c(\theta) + \psi_o , \quad (5)$$

and the osmotic pressure, ψ_o, is given by:

$$\psi_o = \frac{RT}{V_w} \ln(a_w) , \quad (6)$$

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where R is the universal gas constant, T the absolute temperature and a_w the water activity (for pure water $a_w=1$ and hence the osmotic pressure is zero).

When the well-known Pitzer's activity coefficient model is applied the osmotic pressure can be calculated as (see e.g. Englezos and Bishnoin 1988):

$$\psi_o = \nu RTm_l\left(1 + z_+z_-A_1 + m_l\left(\frac{2\nu_m\nu_n}{\nu}\right)A_2 + m_l^2\left(\frac{(2\nu_m\nu_n)^{3/2}}{\nu}\right)\beta_2\right) \quad (7)$$

where

$$A_1 = \frac{A_\phi I^{1/2}}{1+1.2I^{1/2}} \quad (8)$$

$$A_2 = \beta_0 + \beta_1\exp\left(-2I^{1/2}\right) \quad (9)$$

A_Φ is the Debye-Huckel coefficient, m_l the molality of the solution, z+ and z- are ion charges, I the ionic strength of the solution, ν_m and ν_n are the number of moles of ions produced by one mole of the electrolyte (i.e., 2 for NaCl) and β_0, β_1, and β_2 are the given parameters for Pitzer's activity coefficient model.

The osmotic pressure of a NaCl solution is given in Figure 3 as an example as calculated using the Pitzer model. As can be seen the osmotic pressure reaches almost 350 bar for a saturated sodium chloride solution. Hence, due to the presence of soluble salts in a porous material, its effective pore size (i.e., the equivalent pore size for a water saturated system) will decrease as the total macroscopic capillary pressure is increased by the osmotic pressure of the salt. Hence, due to the salts absorbed in the poultice its effective pore size will decrease.
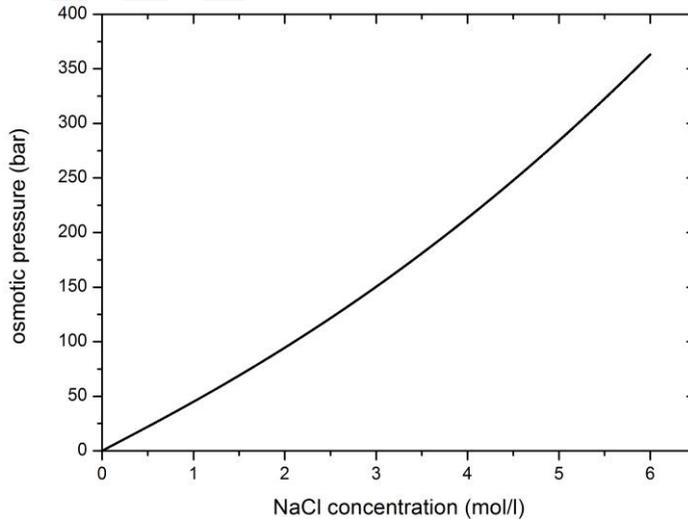
Figure 3. The osmotic pressure of NaCl solution as a function of the concentration as calculated from the Pitzer model.

3. NMR

In this study we have used Nuclear Magnetic Resonance (NMR) to measure non-destructive and quantitative the moisture in the samples while drying. NMR is based on the principle that in a magnetic field, nuclei have a specific resonance frequency and can be excited by a radio frequency field. The resonance frequency f (Hz) depends linearly on the magnitude of the magnetic field:

$$f = \frac{\gamma}{2\pi} B_0 \qquad (10)$$

Where $\gamma/2\pi$ (HzT^{-1}) is the gyromagnetic ratio, B_0 (T) is the main magnetic field. For ^{1}H $\gamma/2\pi$ is 42.58 MHzT^{-1} and ^{23}Na is 11.26 MHzT^{-1}. Therefore, by using a specific frequency the method can be made sensitive to a particular type of nucleus, in this case either hydrogen or sodium. The signal intensity S of a spin echo as used in the experiment is given by:

$$S = \rho \left[1 - \exp\left(-\frac{T_r}{T_1} \right) \exp\left(-\frac{T_e}{T_2} \right) \right] \qquad (11)$$

where S is signal intensity, ρ is the density of the hydrogen nuclei, T_r and T_1 are the repetition time of the pulse sequence and spin-lattice relaxation time, T_e and T_2 are the spin echo time and spin-spin relaxation. To measure the maximum signal, i.e. from all pore sizes, T_e should be as short as possible as T_1 and T_2 are proportional to the pore size. For the presented experiments, a home-built NMR scanner with a static magnetic field of 0.78 T and gradient up to 0.3 T/m is used (Petkovic et al. 2007). To perform quantitative measurements a Faraday shield is placed between the coil and the sample.
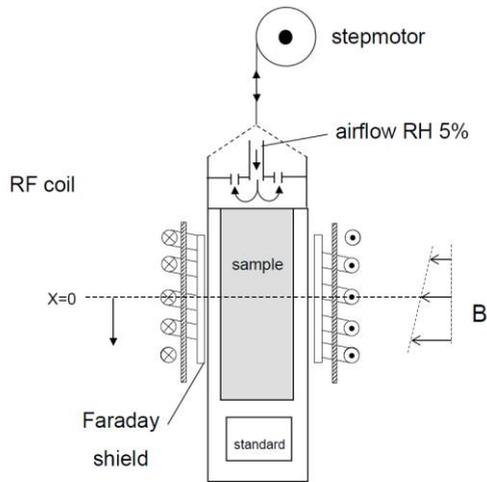
Figure 4. A schematic diagram of the NMR setup for drying experiments. The Teflon holder with the sample and the standard is moved in the vertical direction by means of a step motor.

The experimental set-up is given in Figure 4. The sample, which has a cylindrical shape with a diameter of 20 mm and a length up to of 80 mm, is moved vertically through the magnet with the help of a step motor. It is sealed at all sides, except for the top over which air with a relative humidity of 5% is blown. In this way, a one-dimensional drying process is created. After each measurement the sample is moved in the vertical direction by the step motor. The measurement time for the moisture content at one position is in the order of 1 min. This procedure is repeated until a complete moisture profile has been measured. A time stamp is given to each measurement point.

4. Osmotic pressure influence

In order to show the effect of purely the osmotic pressure we have conducted an experiment where desalinate a Bentheimer with a poultice with the same pore size distribution. If we would only take the capillary pressure into account we would not expect any advection and therefore no desalination effect. In this experiment we have dried a Bentheimer saturated with 5M NaCl solution on top of a 2 M NaCl solution saturated Bentheimer. In this case due to the higher salt concentration the effective pore size of the Bentheimer with 5 M NaCl solution will be smaller because of the osmotic pressure. The resulting measured moisture profiles during drying are given in Figure 5. As can be seen indeed the Bentheimer with 5 M NaCl solution dried more slowly indicating that its effective pore size is smaller due to the osmotic pressure.
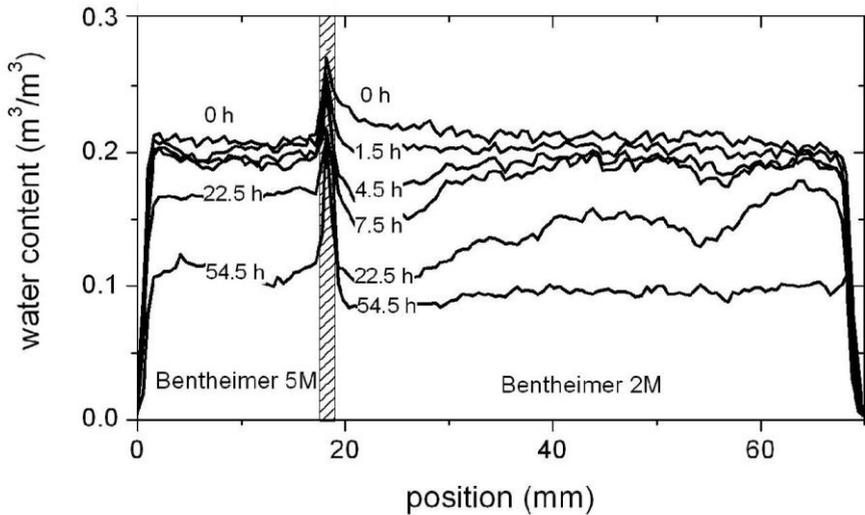
Figure 5. The measured water profiles in a Bentheimer/Bentheimer system for several times during drying. Initially the Bentheimer on the top was saturated with 5M NaCl solution and the substrate Bentheimer was saturated with 2M NaCl solution.

The corresponding moisture content at the interface for this drying experiment is plotted in Figure 6.
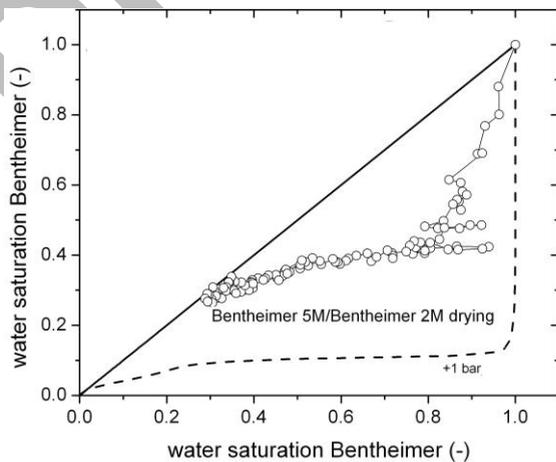
Figure 6: The water saturation of the 2M NaCl solution saturated Bentheimer at the interface as a function of water saturation of the 5M NaCl solution saturated Bentheimer at the interface (see also Figure 5). The solid line represents the relation when both materials are water saturated

whereas the dashed line represents the relation as determined from the capillary pressure curve and the calculated osmotic pressure.

As can be seen, there is a clear deviation from the curve as expected from pure capillary effects. After some time, a deviation can be seen from the relationship as predicted on basis of the calculated osmotic pressure. This is due to the salt transport in the Bentheimer saturated with 2M NaCl solution towards the interface, as a result of which the concentration difference decreased at the interface and the osmotic pressure will change.

5. Conclusions

These drying experiments demonstrate the effect that osmotic pressure has on salt and moisture transport within porous materials. A saline solution in a porous material will exert an osmotic pressure that will to reduce the effective pore size of the material. This study shows that the contribution of osmotic pressure can exert a significant influence on salt extraction using poultices during drying. Importantly, as salt is transported from the substrate and into the poultice, this results in a build-up of osmotic pressure within the poultice, thereby enhancing the extraction.

These findings have potential practical implications for the optimisation of poulticing treatments. While the pore size requirements for advection to take place at the start of the process remain, these constraints need not be quite so severe. They are gradually overcome by the build-up of an osmotic pressure due to the on-going migration of salt from the substrate to the poultice. As a result, the longer a poultice stays in contact with the substrate, the more it will accumulate salt, and thereby the osmotic pressure is increased and its effective pore size will become smaller enhancing the desalination process.

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